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Patents ADP number *(if you know it)*	07764137001
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4. Title of the invention	ORGANIC LIGHT EMITTING DIODES
5. Name of your agent *(if you have one)*	PARLETT, Peter Michael
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SMC 60537

APPLICANTS

AVECIA LIMITED

TITLE

ORGANIC LIGHT EMITTING DIODES

ORGANIC LIGHT EMITTING DIODES

This invention relates to organic light emitting diodes (OLEDs), to a process for their manufacture, particularly to improved techniques that are especially suitable for the low cost fabrication of solution coatable OLEDs by printing, and to their uses.

OLEDs have been attracting growing interest over the past decade. OLEDs are devices that generally comprise an organic electroluminescent material sandwiched between two electrodes. When an electrical current is applied the OLED radiates light generated by recombination of electrons and holes in the electroluminescent material. Plastic OLED devices based on light emitting polymers (LEP) or electroluminescent organic molecules make it possible to produce low cost, large area displays on flexible substrates, especially by solution coating. Low cost manufacturing, however, requires printing techniques that take advantage of the solution coatability of OLEDs.

A number of methods are disclosed in the literature for the manufacture of organic light emitting displays. A recent review can be found in: C.R. Acad.Sci., Ser IV: Phys., Astrophys. (2000), 1(4), 493-508.

For solution processable materials spin coating is routinely employed to give uniform thin films. The patterning of these devices can be achieved by forming a 3D-pixellated insulating structure (wells) on the injecting electrode by photolithography. However, deposition of solutions of electroluminescent materials in these wells can be problematic since the liquid tends to wet the walls of the well and this results in an uneven layer. Light emission and device efficiency of OLEDs is sensitive to this layer thickness, therefore photolithography is not entirely suitable for patterning OLED devices.

Screen-printing has been used to pattern either hole transport materials or emissive polymers. In each case a screen-printing fluid of an active material is prepared and patterned through a preformed mesh using a squeegee (Advanced Materials (2000), 12(17), 1249-1251). This method is not entirely suitable because problems are encountered in obtaining uniform film thickness, transfer of the mesh pattern and feature size resolution. Furthermore, the material to be patterned needs to be of the correct viscosity for screen printing, which is not always possible.

Ink-jet printing of OLED materials has been reported. For example, deposition of Nile Red doped into poly-vinylcarbazole onto a flexible substrate has been reported (Appl. Phys. Letts, 72(5) 519-521). However, uneven polymer distribution within the drops, domed topography of the drops, pin-holing and uneven light emission are reported problems.

The fabrication of OLED devices using the ink-jet deposition of an active material(s) (whether OLED, hole or electron transport material or conductive layer such as polyaniline (PANI) or poly(3,4-ethylenedioxy)thiophene-2,5-diyl (PEDOT) has been reported extensively. In all cases the active material is printed into a preformed pixellated substrate prepared by

standard lithography (e.g. JP 10012377 (SEC); WO9907189 (Cambridge Consultants); WO9912397 (SEC); WO9939373 (Sturm)). Again, the materials need to be formulated into an active ink, which is not always possible.

EP0193820 (Kanegafuchi, 1986) describes a method of forming a thin film pattern by forming a "lift-off layer" onto which the film to be patterned is deposited. The "lift-off layer" can be created by screen-printing or ink jet. The method can be used to pattern metal, silicide, amorphous or crystalline semiconductor, and insulator. Possible applications include solar cell, photo sensor, photoreceptor for electrophotography, thin film diode and transistor. Examples provided are amorphous silicon solar cells. The invention does not teach the manufacture of OLEDs or displays. It does not concern the patterning of solution coatable electroluminescent materials either. Indeed, no OLED display has been reported using these or similar techniques.

Of the above techniques those which take advantage of liquid coatability of organic materials are much preferred. It is especially desirable that non-reactive techniques are used due to the sensitivity of OLED materials to the strong UV light or chemical photoinitiators used in photolithography. Printing techniques, e.g. ink-jet, screen printing or soft lithography (Michel et al, IBM J. Res. & Dev., Vol 45, p697, 2001) hold much promise as the achievable resolution increases for example, by using novel ink-jet head and stamp materials. However, printing by these techniques requires the formulation of an active layer e.g. electroluminescent material into an effective ink. This can be problematic since the active materials are often only soluble in aggressive organic solvents or in acidic aqueous media. These can give rise to material compatibility issues either with the ink-jet head or with the stamp material. Accurate printing requires the adjustment of many parameters such as viscosity, levelling flow and drying properties of the formulation. This is not always easily achievable and soluble OLED materials are also sensitive to additives used in printing processes. Thus there is a need for improved techniques that still rely on printing, for example ink-jet, screen printing or microcontact printing, but resolve some of the issues of formulating OLED materials into inks.

We have recently surprisingly discovered that indirect patterning is a very effective method for the fabrication of OLEDs.

According to the present invention there is provided a method of forming an OLED element or OLED display with one or more layers in which at least one of the layers is patterned by:

a) forming a negative image of the desired pattern on a substrate with a lift-off ink;
b) coating an OLED layer material to be patterned on top of the negative image; and
c) removing the lift-off ink and unwanted areas of the layer to be patterned to leave the desired pattern.

This series of steps can be repeated to build up suitable multi-layer structures, for example to sequentially pattern a hole transport layer, emissive layer and electron transport layer. Or alternatively to pattern multi colour displays by sequentially patterning, for example,

a red, then green, then blue emissive material over a layer and using the negative pattern at each step to mask the area not to be patterned.

In one embodiment of the present invention a multiplicity of layers can be patterned in a single set of printing and lift-off steps using one pattern. This ensures excellent vertical alignment of edges, which would be difficult to achieve by direct printing.

In another embodiment of the present invention a layer of ink is patterned as a blocking layer between two of the OLED layers. This may then be over-coated without removal to prevent conduction in this area of the device, i.e. the lift-off step c) may be omitted. Furthermore, the ink need not be a lift-off ink. The ink may be dark in colour to increase the contrast ratio of the OLED.

The main advantages of the present method are that it:

- provides a way of producing large area OLEDs;
- provides a way of solution coating OLEDs, as opposed to vacuum deposition;
- removes the need for formulating OLED materials into inks;
- avoids registration problems by providing a highly accurate means of printing one layer on top of another;
- allows the creation of new multilayer structures, which is not possible with direct printing techniques;
- provides a means of obtaining good thickness uniformity;
- avoids the need to use additives; and
- avoids formation of pre-defined wells.

These advantages are explained in more detail below.

The present process eliminates several problems associated with the manufacture of OLEDs, for example:

- it is possible to overcome the issue of formulating OLED materials such as polymers or small molecules, blocking layer, injection layer, cathode and anode materials into inks as would be required for direct printing. There is no need to compromise the material by the use of additives or unwanted solvents. The ink can be chosen which is best suited to achieve high resolution and the same ink and print head can be used for defining a variety of layers.
- the deposition technique for the layer material(s) may remain solution coating, but the choice of the techniques is wide because resolution is not now defined by this step.
- the thickness uniformity of the final pattern is excellent, especially at the edges, which is a very important requirement for thin OLED layers in the nanometre range. This is difficult to achieve by direct printing. The use of lithographically patterned wells, with their inherent problems, may be avoided.

- the patterning of small molecule type vapour deposited displays is severely limited by the size of shadow mask that can be effectively created. The current method may increase drastically the size of small molecule displays and provide a printing technique to fabricate them.
- The method provides a means to achieve high accuracy of alignment between layers by simple and cheap printing techniques. The printed pattern can be used to affect lift-off of several layers at the same time. As a result, these layers will 'self align' in a highly effective manner. No direct printing technique has so far achieved such well-aligned overlay of vertical layers. There has been a previously unfulfilled need to print OLEDs at high resolution.
- The use of self-alignment by the combination of print and lift-off makes it possible to achieve new OLED structures by low cost printing, for example multilayer OLEDs or red, green or blue pixels in good alignment.

The method can integrate the patterning of organic light emitting materials (polymer or small molecule), blocking layers, injection or transport layers, cathode and anode materials, display pixel interconnect layers and dopants for organics OLEDs and OLED displays. The process can be fully ambient, and if required, all manufacturing steps can remain based on solution coating. The OLED devices may form part of an active or passive display matrix.

The method can also be used as a complementary tool together with direct patterning techniques for OLEDs, such as those described in the art.

The OLED elements may be used to manufacture multicolour displays, small or large area signs, logos or illuminating features.

The negative image of the desired pattern is preferably formed using a lift-off ink. The lift-off ink is preferably insoluble in the medium used to deposit the layer to be patterned. The lift-off ink medium is preferably a liquid which does not dissolve the layer on which the lift-off ink is printed. The lift-off ink medium can be either aqueous or non aqueous. For example, a water based lift-off ink is suitable on polymer surfaces that are insoluble in water, e.g. polyesters. An advantage is that the lift-off ink does not necessarily need to be electronic grade as it is removed in the process together with the layer to be patterned. The lift-off ink may be flexible in composition and include flow and other additives. When used with screen-printing applications, the lift-off ink can have a very high viscosity, up to 90,000 cp, preferably up to 70,000 cp, and more preferably between 500 and 10,000 cp. But when used with ink-jet printing, the ink viscosity is preferably in the range from about 0.7 to 100 cp, and more preferably from about 3 to 40 cp. The ink preferably has a surface tension from 20 to 70 dynes/cm, more preferably 20 to 60 dynes/cm. This will be governed both by the mode of printing, choice of inkjet printing head and the surface energy of the surface to be printed. Since good edge acuity is required then the surface tension of the lift-off ink relative to the substrate is preferably from 20 to 110deg and more preferably 40 to 80deg. For an inkjet lift-off ink the contact angle with the nozzle plate is preferably from 10 to 150 deg.

The lift-off ink maybe either polar or nonpolar and the liquid medium preferably has a boiling point from 40°C. to 300°C. Preferred liquid media include, but are not limited to, water, alcohol, dioxane, glycols, cyclic amides, toluene, chloroform, tetrahydrofuran, dichlorobenzene, 1,2-dichloroethane, and xylene. The lift-off ink preferably contains from 50% to 99.8% liquid medium, by weight. Liquid medium mixtures are preferred to help control ink application properties such as latency, substrate wetting and drying time.

The lift-off ink may further comprise a colorant, a polymeric binder and functional additives which are used to modify the ink viscosity, surface tension, and latency. Suitable colorants for the lift-off composition include dyes or pigments such as carbon black. Suitable polymeric binders for the lift-off composition include but not limited to acrylics, polyurethanes or silanes.

Cross-linking agents can be included in the lift-off ink to permit cross-linking of the printed ink so as to modify the lift-off parameters (either through partial shrinkage to aid lift-off or to improve solvent resistance to the subsequent coating solution). Cross-linking agents are preferably added to the ink in a concentration in the range from about 0.5 to 30 wt. % of the solid ingredients, and more preferably from about 1 to 10 wt. % of the solid ingredients. Partial shrinkage or microcracks may be induced, for example, by heat curing. This way the efficiency of the lift-off step may be improved by allowing the lift-off solvent to penetrate the ink at the pattern edges or through its surface.

The lift-off ink may be deposited on the substrate by a direct printing technique such as ink-jet printing, screen printing, microcontact printing, stamping, soft lithography or electrophotographic printing using a liquid or solid toner. In each case the ink is formulated to the appropriate viscosity, rheology and surface tension for the specific printing process. The use of ink-jet printing is advantageous because the same ink formulation and ink-jet head may be used, followed by the same chemical or mechanical process for the lift-off step, for the patterning of different layers thereby simplifying the hardware required. The printed lift-off ink is preferably thicker than the layer subsequently deposited onto it, this improves the efficiency of the lift-off step. The lift-off pattern is from 100 nm to 100 μm thick, preferably from 1 μm to 50 μm.

The OLED layer to be patterned may be applied by a variety of coating and printing techniques. Examples include spin-, spray-, dip-, web-, die- or evaporation coating; electroless deposition and ink-jet printing, screen printing, microcontact printing, stamping or soft lithography. When the OLED layer to be patterned is deposited by ink-jet printing, selective deposition on different areas is possible. For example, red, green and blue electroluminescent materials may be deposited on different areas. Subsequently the pattern is defined by the underlying lift-off ink, offering better resolution. In this embodiment, more than one material is patterned by the same lift-off layer deposited in a single printing step.

The thickness of the OLED layer or multiplicity of layers may be from 1nm (in case of a monolayer) to 10 μm, preferably from 1nm to 1μm, more preferably from 1nm to 500nm.

The preferred deposition technique for the OLED layer to be patterned is a liquid coating technique, more preferably spin-, die- or spray-coating.

Once the lift-off ink is printed and the OLED layer to be patterned is deposited above it, the step of lift-off can be carried out by dissolving the lift-off ink using a liquid medium. During this step the lift-off pattern is removed together with parts of the OLED layer to be patterned. Any liquid medium may be employed for this, as long as it dissolves little or none of the OLED layer to be patterned which is on the substrate, or in multilayer devices on an earlier patterned OLED layer. Preferred liquid media include water, alcohols such as methanol and ethanol. Liquid media may be used alone or in combination with other liquid media. The efficiency of the lift-off part of the process may be enhanced by ultrasonic agitation, stirring, spraying liquid medium and/or heating. The lift-off part of the process may be optionally effected by abrasion, high pressure air or other mechanical action.

Various substrates may be used for the fabrication of OLEDs, plastics materials are preferred and examples include alkyd resins, allyl esters, benzocyclobutenes, butadiene-styrene, cellulose, cellulose acetate, epoxide, epoxy polymers, ethylene-chlorotrifluoro ethylene, ethylene-tetra-fluoroethylene, fibre glass enhanced plastic, fluorocarbon polymers, hexafluoropropylenevinylidenefluoride copolymer, high density poly-ethylene, parylene, polyamide, polyimide, polyaramid, polydimethylsiloxane, polyethersulphone, polyethylene, polyethylenenaphthalate, polyethyleneterephthalate, polyketone, polymethylmethacrylate, polypropylene, polystyrene, polysulphone, polytetrafluoroethylene, polyurethanes, polyvinylchloride, silicone rubbers, silicones. Preferred substrate materials are polyethyleneterephthalate, polyimide, and polyethylenenapthalate. The substrate may be any plastic material, metal or glass coated with the above materials. The substrate should preferably be homogenous to ensure good pattern definition.

The wetting of the ink formulation may be optimised by the surface treatment of the substrate, for example, by plasma treatment. Such treatment may also be used to enhance adhesion of the layer to be patterned to the substrate or improve edge acuity. As a result, the lift-off of the ink together with the layer above may be more efficient. The technique can be further optimised by using intermediate layers coated between the ink pattern and the layer to be patterned. Such layers can be used as barriers stopping the diffusion of ink into other layers.

The OLED comprises an anode, a cathode and an electroluminiscent layer. The OLED optionally comprises other layers such as an electron blocking layer(s) (or hole injection electrode(s)), a hole injection layer(s), a hole transport layer(s), a hole blocking layer(s) (or electron injection layer(s)), electron transport layer(s), an electron injection electrode(s), a dopant or an insulator(s).

The electroluminescent layer is made up of substantially organic or organometallic electroluminescent materials. Suitable materials include organic photo- or electroluminescent, fluorescent and phosphorescent compounds of low or high molecular weight. Suitable low molecular weight compounds include, but are not limited to, substituted 9,9' spirobifluorenes

(EP 0676461), Alq3 (an aluminum complex formed by coordination of three molecules of hydroxyquinoline with an aluminum atom), lanthanide complexes such as those of europium and ytterbium (WO 9858037), triplet emitters such as $Ir[2\text{-}PhPy]_3$. Suitable high molecular weight materials include polymers preferably those having substantially conjugated backbone (main chain), such as polythiophenes, polyphenylenes, polythiophenevinylenes, polyphenylenevinylenes, polyalkylfluorenes. In the present invention the term polymer includes homopolymer, copolymer, terpolymer and higher homologous as well as oligomers. Examples of such mateials are given in US 5708130, WO97/39082, WO96/10598.

The electroluminescent layer preferably has an average thickness of from 50 to 200nm, more preferably from 60nm to 150nm.

The electron blocking layer (hole injection electrode) is suitably made of a metal or an alloy having a high work function such as Au, Pt, Ag. Preferably, a more transparent electron blocking layer (hole injection electrode) material such as an indium tin oxide (ITO) is used. Conductive polymers such as polyaniline (PANI) and a poly-3,4-ethylenedioxythiophene (PEDOT) are also suitable transparent hole-injection electrodes. Preferably, the electron blocking layer (hole injection electrode) has a thickness of from 50 to 300nm.

Hole-injecting and hole-transporting layer materials include soluble phthalocyanine compounds, triarylamine compounds, electroconductive polymers, perylene compounds, and europium complexes.

Electron-injecting (hole blocking) and electron-transporting layer materials include Alq3, azomethine zinc complexes, and distyrylbiphenyl derivatives. These are however not exhaustive.

The electron injection electrode is preferably made of a metal or an alloy having a low work function, such as Yb, Ca, Al, Mg:Ag, Li:Al, Ba or is a laminate of different layers such as Ba/Al or Ba/Ag electrode.

Dopants used in the invention may be compounds such as 3-(2-Benzothiazolyl)-7-diethylaminocoumarin (Coumarin 6), europium complexes, ruthenium complexes, Rhodamine salts, platinum complexes, iridium complexes and Nile red although this list is not exhaustive.

Insulators used in the invention may be inorganic or organic or a composite of the two. It is preferred that the insulator is solution coated enabling ambient processing. When the insulator is being patterned, it may perform the function of a blocking layer between OLED materials. The insulator may be any organic polymer or polymer precursor, optionally containing inorganic particles. The insulator can be spray-, dip-, web- or spin coated or deposited by any liquid coating technique. Any liquid carrier may be employed as long as it does not dissolve the lift-off ink.

The invention will now be further described by way of example and with reference to the accompanying drawings in which:

Figure 1 shows indirect printing by ink-jet, stamping and microcontact printing;

Figure 2a) shows a profile of material printed directly on a flat substrate;

Figure 2b) shows a pre-patterned well on a flat substrate;

Figure 3 shows indirect printing to create a negative pattern;
Figure 4 shows the patterning of an ink which is used to block the movement of charge into the electroluminescent layer;
Figure 5 shows the patterning of a conductive polymer to create a patterned OLED;
Figure 6 shows the patterning of an anode and cathode layer to create a patterned OLED;
Figure 7 shows printing and lift-off used to define the electroluminescent material itself into pixels;
Figure 8 shows the lift-off method may be used to pattern self-assembled monolayers (SAMs);
Figure 9 shows a pattern printed onto PEDOT using ink that serves as a blocking layer;
Figure 10 shows the areas of PEDOT which had no ink upon them emitting light with all other areas blocked by the ink-jet printed layer;
Figure 11 shows an ink pattern printed onto ITO coated polyester; and
Figure 12 shows a pattern printed onto a substrate using an ink-jet printer

The process comprises printing a negative ink pattern as shown in Figure 1, applied for example by ink-jet (1a), soft lithography (1b) or screen-printing (1c), onto a surface. The OLED layer to be patterned is then spin (3a), spray (3b), or dip (3c), web, ink-jet coated, or evaporated on top of the ink pattern (2). Subsequently the ink and the unwanted material can be removed using a lift-off process. Thus the negative pattern coating may be used to remove unwanted parts of an OLED device and a sequence of patterned layers can be built up. The direct printing combined with lift-off match very well the liquid coating steps e.g. spin coating employed in OLED display manufacture. Related techniques are described in the prior art, however, they have never been used for the manufacture of OLED's. The most attractive feature of OLEDs is the possibility to manufacture them under ambient conditions. The combination of print & lift-off patterning ("L-Print") used with OLED materials enables the printing of OLED devices by fully ambient processing, which has not been envisaged elsewhere.

The present invention uses the combination of a printing step and a lift-off step to pattern elements of an OLED. Instead of formulating the material itself into an ink, we have printed a negative pattern with a separate, specially selected lift-off ink. High quality OLEDs can be fabricated by this simple technique. The method is well suited to wet processing of organic displays. Using the same ink for many different constituent layers is highly advantageous as it reduces the complexity of the process. If desired all processes can be based on liquid processing in a non-reactive manner. Further advantage of the indirect process is that the uniformity of the thickness of the printed pattern is not important – unlike when using a direct printing approach. The printed lift-off pattern will provide excellent edge definition even when the printed area is thin at its edges. A serious problem in printing light-emitting polymers (LEPs) directly is to achieve uniform thickness of around 70 – 100 nm. As is shown schematically in Figure 2a, ink-jet droplets (11) of LEPs will deposit depending on the contact angle with the surface (12) and there is normally a greater thickness in the middle

of the deposited pixel. Likewise spin coated films upon pre-defined well structures (Figure 2b) result in pixels of the polymer that are thicker at the edge than in the middle due to the solution wetting the edges of the well. These prior art techniques for solution depositing LEPs result in variable light emission from different areas of the pixel. Since in the present technique (shown in Figure 3) patterning on a substrate (22) is achieved by the use of the lift-off ink (21), this problem is greatly reduced because the LEP (23) itself is deposited by spin, spray, or web coating on a largely flat topography and thus achieves superior layer uniformity. The uniformity of other layers in the OLED device, for example the hole injection layer, will have a similar effect upon device performance therefore it would be advantageous to pattern these layers using lift-off rather than via prior art techniques.

This series of steps can be repeated to build up suitable multi-layer structures, for example to sequentially pattern a hole transport layer and electron transport layer. Alternatively to pattern multi colour displays by sequentially patterning, for example, a red, then green, then blue emissive material over a layer and using the negative pattern at each step to mask the area not to be patterned.

In one embodiment of the present invention a multiplicity of layers can be patterned in a single set of printing and lift-off steps using one pattern. This ensures excellent vertical alignment of edges, which would be difficult to achieve by direct printing.

In another embodiment of the present invention a layer of ink is patterned as a blocking layer between two of the OLED layers. This may then be over-coated without removal to prevent conduction in this area of the device. The ink may be dark in colour to increase the contrast ratio of the OLED.

Using the present method high conductivity metal layer can be incorporated into a fully printed OLED, this has previously been done only by lithography or shadow mask evaporation. The invention also makes it possible to pattern metal dispersions, colloidal metal suspensions or precursor metal solutions using a lift-off ink. The liquid medium based metal systems themselves may be spin, spray, web or dip coated.

OLED displays may benefit from doping the light emitting material or a contact region. The present invention provides means to perform doping in a controlled, patterned manner. A separate negative layer can be printed for the lift-off of a dopant. The dopant itself may be coated uniformly over the entire area of the display.

Figure 4 shows the patterning of an ink which is used to block the movement of charge into the electroluminescent layer, thereby allowing a patterned OLED to be constructed. A layer of metal (42) forming an anode is deposited on a substrate (41) by evaporation or sputtering. A conductive polymer layer (43) is then applied by spin coating. The blocking ink (44) is patterned in areas where the device is not to emit light. Following this the electroluminescent layer (45) is deposited by spin coating or evaporation on top of the ink. Finally a cathode layer is deposited (46). Alternative examples can be envisaged where the blocking ink is deposited upon a different layer of the device such as the electroluminescent layer or anode.

Figure 5 demonstrates the patterning of a conductive polymer to create a patterned OLED. The anode material (52) is first deposited upon the substrate (51) followed by the lift-off ink (53). The conductive polymer (54) is spin coated on top and lifted-off to produce a pattern. The EL layer (55) is evaporated or spin-coated on the patterned polymer and finally a cathode layer (56) is deposited. The charge injection into the EL layer is considerably more efficient in the areas over-coated with conductive polymer therefore the device emits light in these areas.

Figure 6 shows the patterning of an anode layer to create a patterned OLED. A lift-off ink (62) is deposited upon a substrate (61) followed by the deposition of an anode layer (63). The ink is then removed with the over-coated layer to leave a patterned anode. Following this a conductive polymer layer (64), EL layer (65) and cathode layer (66) are deposited to complete the device. Alternative examples can be envisaged where the cathode layer is patterned and the device is fabricated in reverse.

In a further embodiment, printing and liftoff may be used to define the electroluminescent material itself into pixels as shown in Figure 7. First an ink pattern 72 is printed on substrate 71 followed by the deposition of electroluminescent layer 73 either by vacuum evaporation or spin coating. Following liftoff; pixels of 73 will remain on the substrate where ink has not been printed. The substrate now may be printed again with a new negative pattern 74 which also covers the pixels. In the next step an electroluminescent material of a different colour 75 is deposited. After a second liftoff step, pixels of two different colours 73 and 75 remain on the substrate as shown in Figure 7e. The process repeated the third time leads to a three colour pixel structure of 73,75 and 76 as shown in Figure 7f.

The lift-off method can be used to pattern self-assembled monolayers (SAMs). This is used to pattern thick polymer layers (>200nm) or materials with a high molecular weight. Referring to Figure 8, the ink is printed on a surface (1) that can be reacted with molecules that form SAMs. Such a surface may be for example ITO (Indium Tin Oxide), metals (such as gold, silver, or aluminium), metal oxides (such as aluminium oxide) semiconductors (such as Si), semiconductor oxides (such as SiO_2), or an insulator. Suitable SAM molecules (2) can be anything that will covalently (or otherwise) bond with the surface and have a terminal functionality that promotes wetting (such as OH, COOH) or de-wetting (such as CH_3, CF_3) of the polymer to be patterned. The surface is reacted with the SAM either by immersing in a solution of the molecules, placing in a vapour stream of the molecules, or bringing into contact with a planar elastomeric stamp (3) such as polydimethysiloxane (PDMS) which has been coated with the molecules from solution. Once the SAM has formed, the ink and loosely bound molecules are lifted-off by immersing in a solvent to produce the patterned SAM (4). Optionally the areas of metal left bare by the lift-off procedure can be further reacted with a SAM (5) which contains a terminal functionality that has the opposite wetting (i.e. high or low surface energy) to the SAM that has been patterned. This will prevent the non-patterned surface from becoming dirty in air. The surface is then coated with a solution of the polymer to be patterned. By tilting the surface, excess polymer will run off the hydrophobic areas and

selectively wet the hydrophilic areas. Removal of the excess polymer can also be achieved by other means (such as spin, bar, or doctor-blade coating). After solvent evaporation the SAM may be removed by plasma or ozone treatment to allow coating of the ITO underneath.

This method of patterning SAMs may be used to alter the electrical properties of a metal or ITO surface. For example, it may be used to alter the work function or to act as a blocking layer. This can then be used to create a patterned OLED or, as in the above description to pattern a polymer layer that would prevent charge in injection into the OLED emissive material.

Example 1.

An ITO coated polyester substrate was cleaned in an air plasma for 20s using a voltage of 5kV. Following this, a water dispersion of poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT) (Baytron P CH8000) was deposited and spun at 1000 rpm for 20s to give a layer of approximately 100nm in thickness. This was dried in an oven at 100 °C for 5 minutes. The pattern (Figure 9) was printed onto the PEDOT using ink that served as a blocking layer. After printing on the PEDOT the sample was baked at 100 °C for 1 minute. A quantity of "super yellow" PPV (Covion SY-17) formulated at 0.5% (wt.) in toluene was deposited on the substrate and spun at 1000 rpm for 30s to give an approximately 70 nm layer. The sample was dried at 100 °C for 20 minutes to evaporate the solvent. The aluminium cathode was deposited onto the sample by thermal evaporation of the metal, through a plastic shadow mask, under vacuum. To test the efficiency of patterning, contacts were made to the ITO and aluminium and the appropriate connections made to a function generator which supplied a 20V square wave signal at low frequency (~5 Hz). The areas of PEDOT which had no ink upon them emitted light (as shown in Figure 10), all other areas were blocked by the ink-jet printed layer. This demonstrates a method whereby an OLED is patterned using a standard inkjet ink but has the added advantage of creating extra contrast due to the black background.

Example 2

The ink pattern (Figure 11) was printed onto ITO coated polyester using an EPSON C60 ink-jet printer. This was left to air dry for 1 hour. A dispersion of conductive PANI in xylene was spin coated onto this patterned ITO at 500 rpm for 3 s and then 4000 rpm for 10 s to give a layer thickness of approximately 100 nm. The sample was immediately sonicated in methanol for 30 s to remove the areas of PANI deposited upon the ink followed by blow drying and baking for 2 minutes at 100 °C. A quantity of "super yellow" PPV (Covion SY-17) formulated at 0.5% (wt.) in toluene was deposited on the substrate and spun at 1000 rpm for 30s to give an approximately 70 nm layer. The sample was dried at 100 °C for 20 minutes to evaporate the solvent. The aluminium cathode layer was deposited onto the sample in several areas by thermal evaporation of the metal, through metal washers, under vacuum. To test the efficiency of patterning, contacts were made to the ITO and aluminium and the

appropriate connections made to a function generator which supplied a 20V square wave signal at low frequency (~5 Hz). Light was emitted from the areas that corresponded to the patterned PANI. This demonstrates the ability of the ink-jet lift-off method to create pixels of light by patterning the charge injection layer of an OLED.

Example 3

Initially a pattern (shown in figure 12) was printed onto a substrate using an Epson C60 ink-jet printer. This was placed in a Cressington sputter coater and 4nm of Pt/Pd metal was deposited onto the whole sample. Lift-off of the ink and undesired metal was achieved by sonication in methanol for 30 s after which the sample was rinsed in methanol and finally blown dry. Any remaining methanol was removed by baking at 100 °C for 1 minute. Following this, PEDOT (Baytron P CH8000) was deposited and spun at 1000 rpm for 20s to give a layer of approximately 100nm in thickness. This was dried in an oven at 100 °C for 5 minutes. A solution of "super yellow" PPV (Covion SY-17) formulated at 0.5% (wt.) in toluene was deposited on the substrate and spun at 1000 rpm for 30s to give an approximately 70 nm layer. The sample was dried at 100 °C for 20 minutes to evaporate the solvent. The aluminium cathode was deposited onto the sample by thermal evaporation of the metal, through a plastic shadow mask, under vacuum. To test the efficiency of patterning, contacts were made to the ITO and aluminium and the appropriate connections made to a function generator which supplied a 20V square wave signal at low frequency (~5 Hz). The areas of patterned Pt/Pd emitted light (note the dot over the i in Avecia did not light as it was not in electrical contact with the rest of the pattern). This demonstrates the ability of the ink-jet lift-off method for patterning the metal anode in OLEDs.

CLAIMS

1. A method of forming an OLED element or OLED display with one or more layers in which at least one of the layers is patterned by:
   a) forming a negative image of the desired pattern on a substrate with a lift-off ink;
   b) coating an OLED layer material to be patterned on top of the negative image; and
   c) removing the lift-off ink and unwanted areas of the layer to be patterned to leave the desired pattern.

2. A method of forming an OLED element or OLED display as claimed in claim 1 wherein the lift-off ink is insoluble in the medium used to deposit the layer to be patterned.

3. A method of forming an OLED element or OLED display as claimed in either claim 1 or 2 wherein the lift-off ink medium is a liquid which does not dissolve the layer on which the lift-off ink is printed.

4. A method of forming an OLED element or OLED display as claimed in any one preceding claim wherein the lift-off ink is deposited on the substrate by a direct printing technique including ink-jet printing, screen printing, microcontact printing, stamping, soft lithography or electrophotographic printing using a solid or liquid toner.

5. A method of forming an OLED element or OLED display as claimed in any one preceding claim wherein the printed lift-off ink is thicker than the layer subsequently deposited onto it.

6. A method of forming an OLED element or OLED display as claimed in claim 5 wherein the printed lift-off ink is from 100 nm to 100 μm thick, preferably from 1 μm to 50 μm.

7. A method of forming an OLED element or OLED display as claimed in any one preceding claim wherein the lift-off ink is deposited by screen printing and has a viscosity up to 90,000 cp, preferably up to 70,000 cp, and more preferably from 500 to 10,000 cp.

8. A method of forming an OLED element or OLED display as claimed in any one of claims 1 to 6 wherein the lift-off ink is deposited by ink-jet printing and has a viscosity in the range from about 0.7 to 100 cp, and more preferably from about 3 to 40 cp.

9. A method of forming an OLED element or OLED display as claimed in any one preceding claim wherein the lift-off ink has a surface tension from 20 to 70 dynes/cm, preferably 20 to 60 dynes/cm.

10. A method of forming an OLED element or OLED display as claimed in any one preceding claim wherein the surface tension of the lift-off ink relative to the substrate is from 20 to 110deg and preferably 40 to 80deg.

11. A method of forming an OLED element or OLED display as claimed in any one preceding claim wherein the lift-off ink contains from 50% to 99.8% liquid medium, by weight.

12. A method of forming an OLED element or OLED display as claimed in any one preceding claim wherein the lift-off ink further comprises a colorant, a polymeric binder or one or more functional additives.

13. A method of forming an OLED element or OLED display as claimed in any one preceding claim wherein the lift-off ink further comprises a cross-linking agent to permit cross-linking of the printed ink.

14. A method of forming an OLED element or OLED display as claimed in any one preceding claim wherein partial shrinkage or microcracks are induced to allow a lift-off solvent to penetrate the ink at the pattern edges or through its surface to aid the lift-off step.

15. A method of forming an OLED element or OLED display as claimed in any one preceding claim wherein the OLED layer to be patterned is applied by spin-, spray-, dip-, web-, die- or evaporation coating.

16. A method of forming an OLED element or OLED display as claimed in any one of claims 1 to 14 wherein the OLED layer to be patterned is applied by electroless deposition, ink-jet printing, screen printing, microcontact printing, stamping or soft lithography.

17. A method of forming an OLED element or OLED display as claimed in any one preceding claim wherein the thickness of the OLED layer or multiplicity of layers is from 1nm to 10 μm, preferably from 1nm to 1μm, more preferably from 1nm to 500nm.

18. A method of forming an OLED element or OLED display as claimed in any one preceding claim wherein the step of lift-off includes dissolving the lift-off ink using a liquid medium.

19. A method of forming an OLED element or OLED display as claimed in claim 18 wherein the liquid medium dissolves little or none of the OLED layer to be patterned.

20. A method of forming an OLED element or OLED display as claimed in any one preceding claim wherein the lift-off step further includes ultrasonic agitation, stirring, spraying liquid medium and/or heating.

21. A method of forming an OLED element or OLED display as claimed in any one preceding claim wherein the wetting of the ink is effected by a surface treatment of the substrate.

22. A method of forming an OLED element or OLED display as claimed in any one preceding claim wherein the OLED layer to be patterned is an anode, a cathode or an electroluminiscent layer.

23. A method of forming an OLED element or OLED display as claimed in claim 22 wherein the electroluminescent layer comprises a substantially organic or organometallic electroluminescent material.

24. A method of forming an OLED element or OLED display as claimed in claim 23 wherein the electroluminescent layer comprises a polymer or oligomer containing monomers of thiophene, phenylene, thiophenevinylene, phenylenevinylene, or fluorene, including substituted forms thereof.

25. A method of forming an OLED element or OLED display as claimed in any one of claims 1 to 21 wherein the OLED layer to be patterned is a hole injection electrode, hole injecting layer, hole transporting layer, electron injection electrode, electron injecting layer or electron transporting layer or interconnect.

26. A method of forming an OLED element or OLED display as claimed in any one of claims 1 to 21 wherein the OLED layer to be patterned is a dopant or an insulator.

27. A method of forming an OLED element or OLED display as claimed in any one preceding claim wherein a multiplicity of OLED layers is patterned in a single set of printing and lift-off steps using one pattern.

28. A method of forming an OLED element or OLED display, the method comprising forming a layer of ink patterned as a blocking layer between two layers of the OLED element or display to prevent conduction in desired areas of the OLED element or display.

SMC 60537

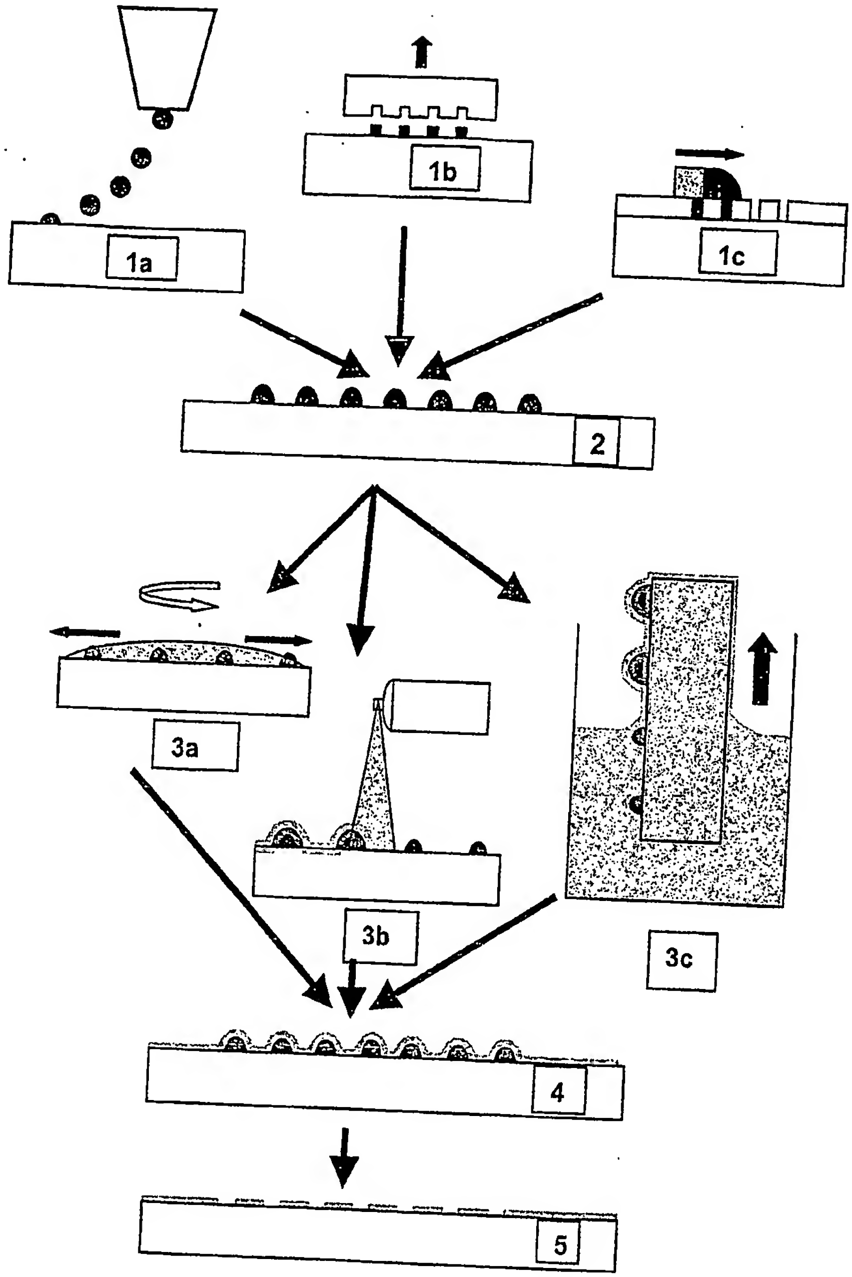

Figure 1

Prior art direct printing

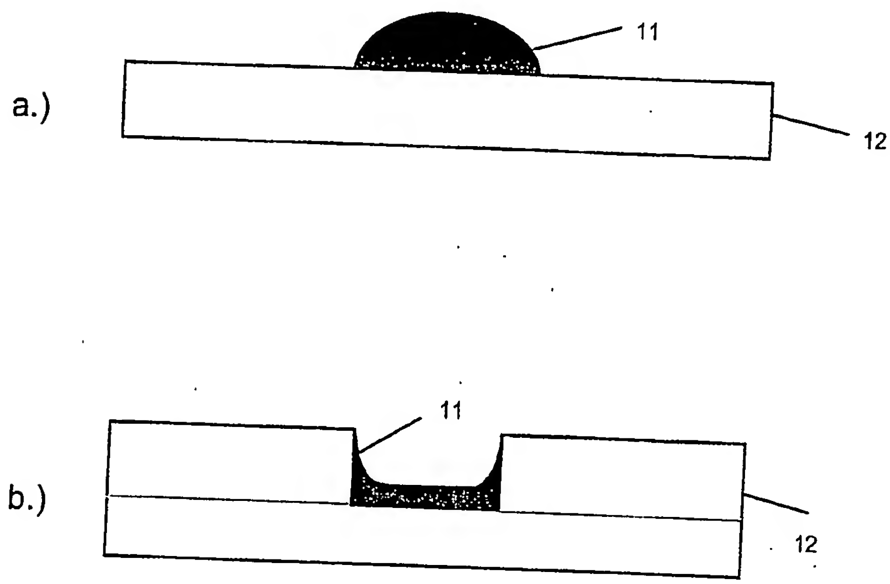

Figure 2

indirect printing

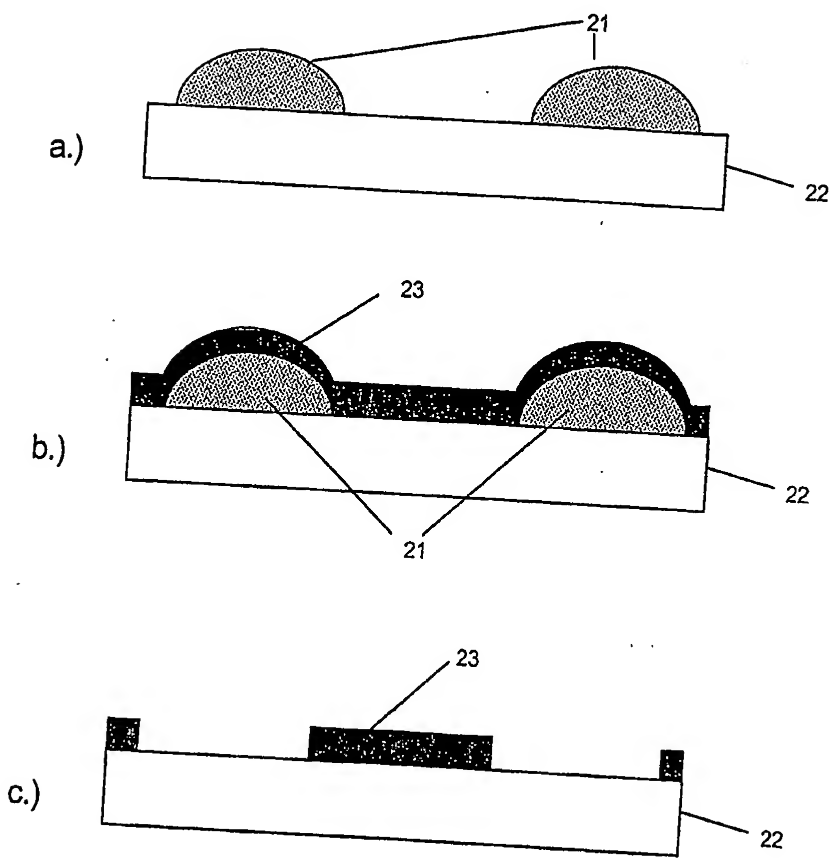

Figure 3

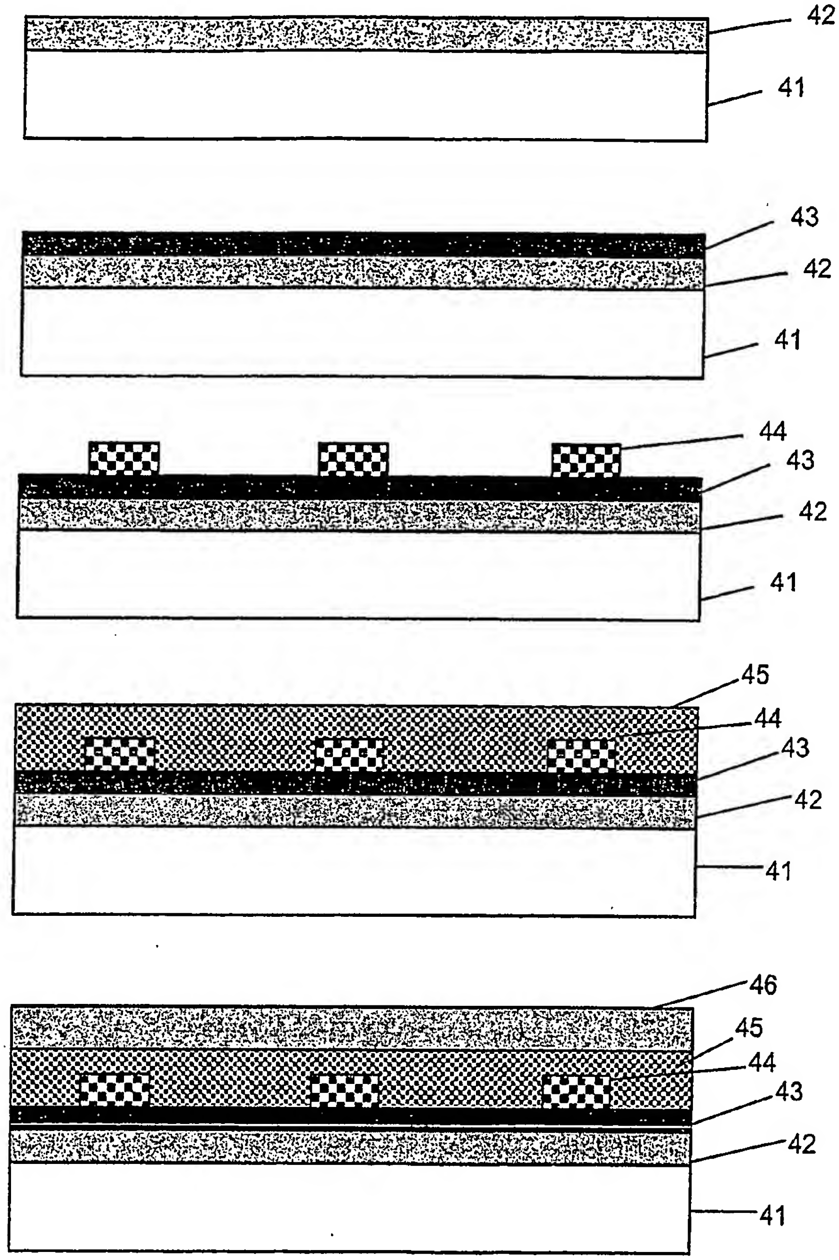

Figure 4

Patterning the injection layer

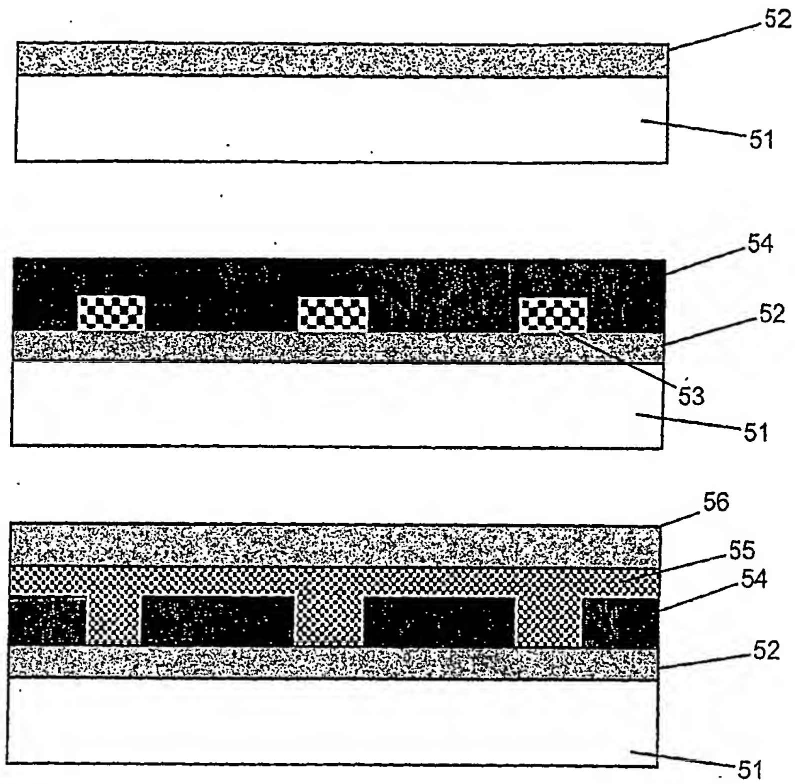

Figure 5

Patterning of anode or cathode

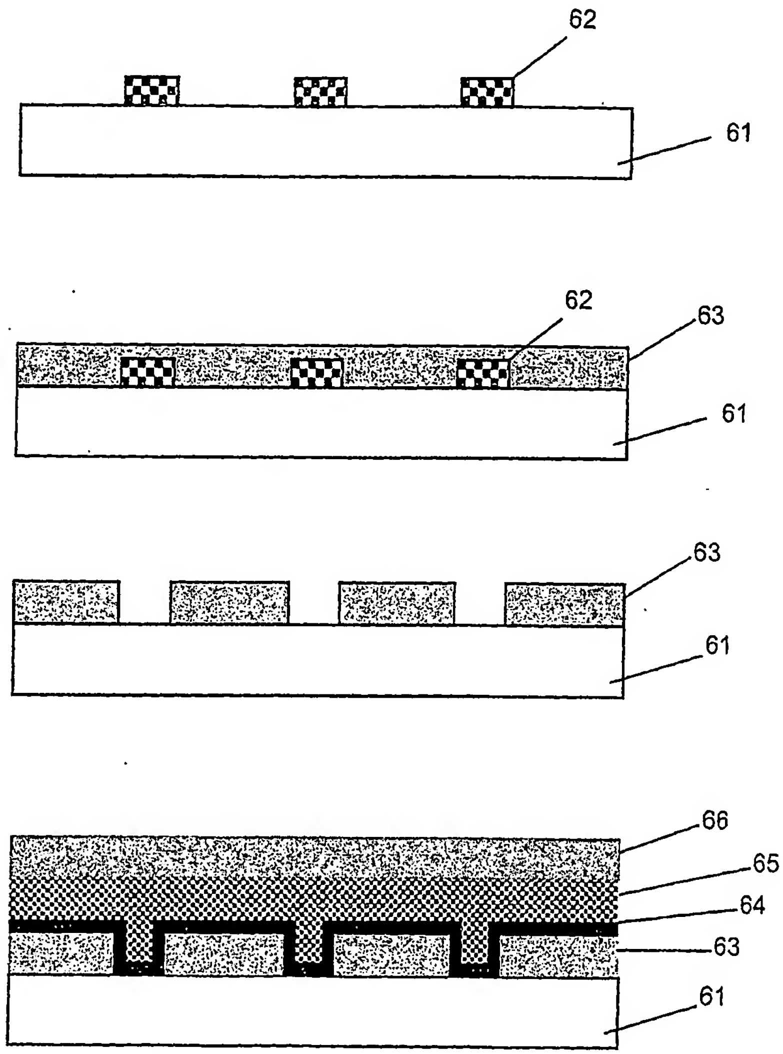

Figure 6

Patterning of Electroluminescent material

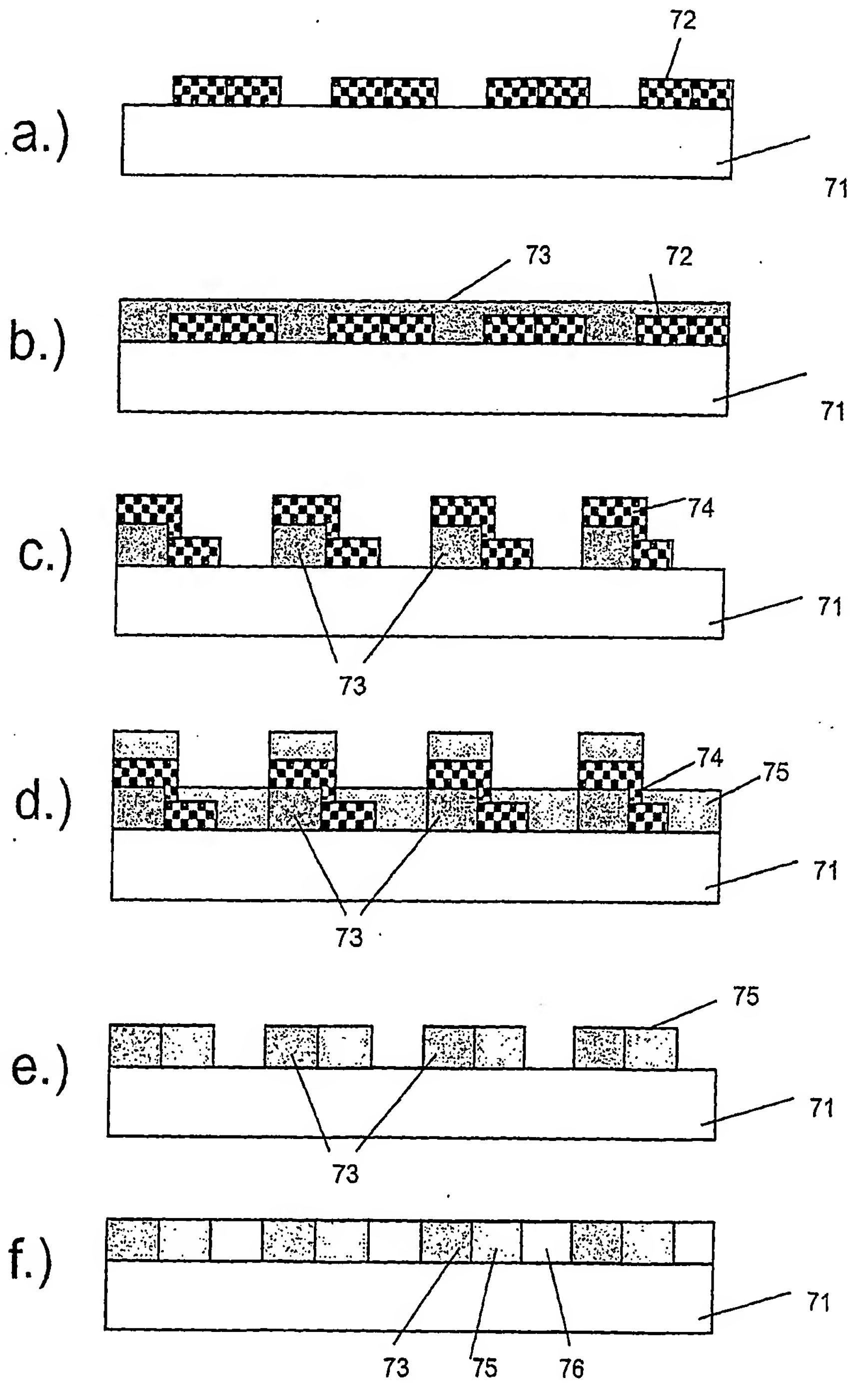

Figure 7

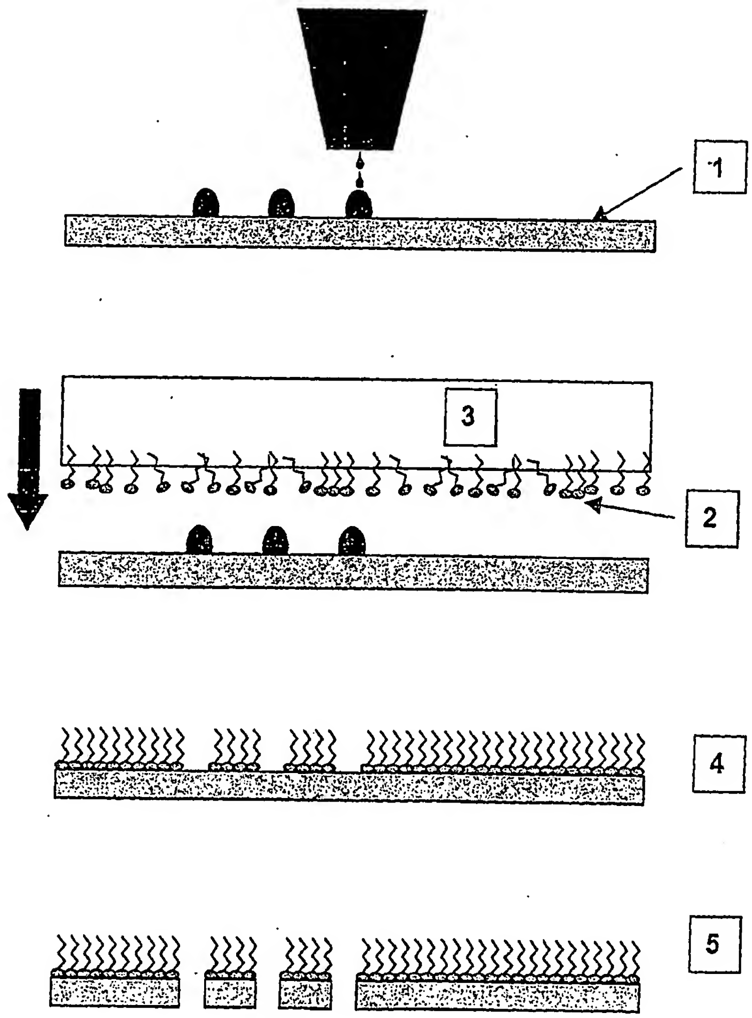

Figure 8

Figure 9

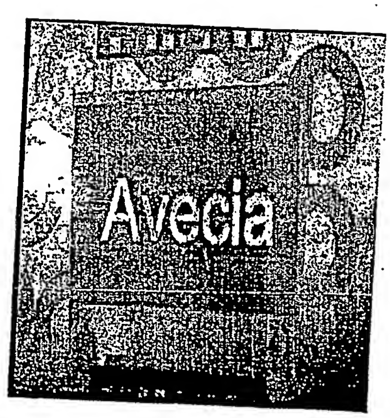

Figure 10

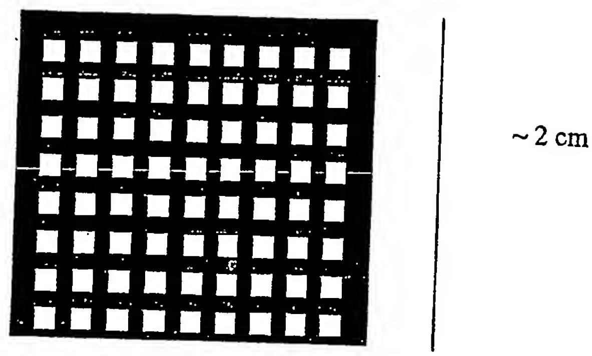

Figure 11

Figure 12

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The Patent Office

Cardiff Road
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1. Your reference	SMC 60537/GB/P1
2. Patent application number *(The Patent Office will fill in this part)*	0218202.0
3. Full name, address and postcode of the or of each applicant *(underline all surnames)*	Avecia Limited Hexagon House Blackley Manchester, M9 8ZS United Kingdom
Patents ADP number *(if you know it)*	07764137001
If the applicant is a corporate body, give the country/state of its incorporation	GB
4. Title of the invention	ORGANIC LIGHT EMITTING DIODES
5. Name of your agent *(if you have one)*	PARLETT, Peter Michael
"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*	Avecia Limited PO Box 42, Hexagon House Blackley Manchester, M9 8ZS United Kingdom
Patents ADP number *(if you know it)*	7764137002

	Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*
6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number			

	Number of earlier application	Date of filing *(day / month / year)*
7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application		

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:* *a) any applicant named in part 3 is not an inventor, or* *b) there is an inventor who is not named as an applicant, or* *c) any named applicant is a corporate body.* *See note (d))*	Yes

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

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Description	12
Claim(s)	03
Abstract	
Drawing(s)	10 -fro

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Priority documents	
Translations of priority documents	
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
Request for preliminary examination and search *(Patents Form 9/77)*	1
Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Signature [signature] Date 5/8/02

Avecia Limited Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom

Mrs K.M. Pinder/Miss G. Terry 0161 721 1361/2

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